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(51) International Patent Classification ⁶ : C07C 217/90, C07F 19/00, 7/00, 7/28, C08F 4/64, 297/08	A3	(11) International Publication Number: WO 98/46651 (43) International Publication Date: 22 October 1998 (22.10.98)
(21) International Application Number: PCT/US98/07466 (22) International Filing Date: 9 April 1998 (09.04.98) (30) Priority Data: 08/843,161 11 April 1997 (11.04.97) US (71) Applicant: MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). (72) Inventors: SCHROCK, Richard, R.; 15 Cabot Street, Winchester, MA 01890 (US). BAUMANN, Robert; 28A Plymouth Street, Cambridge, MA 02139 (US). (74) Agent: OYER, Timothy, J.; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).		(81) Designated States: AU, CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> (88) Date of publication of the international search report: 25 March 1999 (25.03.99)
(54) Title: LIVING OLEFIN POLYMERIZATION PROCESSES (57) Abstract Processes for the living polymerization of olefin monomers with terminal carbon-carbon double bonds are disclosed. The processes employ initiators that include a metal atom and a ligand having two group 15 atoms and a group 16 atom or three group 15 atoms. The ligand is bonded to the metal atom through two anionic or covalent bonds and a dative bond. The initiators are particularly stable under reaction conditions in the absence of olefin monomer. The processes provide polymers having low polydispersities, especially block copolymers having low polydispersities. It is an additional advantage of these processes that, during block copolymer synthesis, a relatively small amount of homopolymer is formed.		

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/07466

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C217/90 C07F19/00 C07F7/00 C07F7/28 C08F4/64
C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C07C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	BAUMANN R ET AL: "SYNTHESIS OF TITANIUM AND ZIRCONIUM COMPLEXES THAT CONTAIN THE TRIDENTATE DIAMIDO LIGAND, ((T-BU-D6)N-O-C6H4)2O2- (NON2-) AND THE LIVING POLYMERIZATION OF 1-HEXENE BY ACTIVATED NONZrME2" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 119, 2 June 1997, page 3830/3831 XP002072608	1-8
P,X	see the whole document see page 3831, column 2, line 12 - line 14 --- -/--	41

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

25 January 1999

Date of mailing of the international search report

02. 02 99

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INTERNATIONAL SEARCH REPORT

In tional Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>WO 97 42197 A (SOD CONSEILS RECH APPLIC ;CENTRE NAT RECH SCIENT (FR); BERTRAND GU) 13 November 1997 see page 2, line 1 - page 3, line 8 see page 4, line 25 - line 31 see page 4, line 3 - page 5, line 4 see examples 1-5</p> <p style="text-align: center;">---</p>	1,9,10, 12
X	<p>CLOKE F G N ET AL: "ZIRCONIUM COMPLEXES INCORPORATING THE NEW TRIDENTATE DIAMIDE LIGAND (ME₃SI)N CH₂CH₂N(SIME₃)₂₂-(L);THE CRYSTAL STRUCTURES OF ZR(BH₄)₂L AND ZRCI CH(SIME₃)₂L" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS, no. 1, 7 January 1995, pages 25-30, XP002048801 see abstract see compound 1, page 28, column 2, paragraph 3 see compound 4, page 29, column 1, paragraph 3</p>	1,9,10, 12-14
A	<p>see page 28, column 2, line 8 - line 10</p> <p style="text-align: center;">---</p>	41
X	<p>CLARK H C S ET AL: "Titanium(IV) complexes incorporating the aminodiamide ligand '(SiMe₃) N{CH₂CH₂N(SiMe₃)₂!(L);the X-ray crystal structures of 'TiMe₂(L)! and 'TiCl{CH(SiMe₃)₂!(L)!" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 501, no. 1, 4 October 1995, page 333-340 XP004023769 see abstract see page 334, column 1</p> <p style="text-align: center;">---</p>	1,9,10, 12-14
X	<p>HORTON ANDREW D: "Cationic alkylzirconium complexes based on a tridentate diamide ligand: new alkene polymerization catalysts" ORGANOMETALLICS, vol. 15, 1996, pages 2672-2674, XP002072479 see abstract see page 2672, column 2, paragraph 1 see page 2673, column 2, paragraph 5 - page 2674, column 2</p> <p style="text-align: center;">---</p>	1,9,10, 12-14
A	<p>PATENT ABSTRACTS OF JAPAN vol. 096, no. 007, 31 July 1996 & JP 08 081415 A (UBE IND LTD), 26 March 1996 see abstract</p> <p style="text-align: center;">---</p> <p style="text-align: center;">-/--</p>	1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/07466

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 21700 A (EXXON CHEMICAL PATENTS INC) 29 September 1994 see example 9	15
X	see column 1; table 1 ---	37
Y	SILVESTRO DI G ET AL: "POLYMERIZATION OF PROPENE WITH ENANTIOMORPHIC SITE CATALYSTS, 1 A STATISTICAL ANALYSIS" MACROMOLECULAR CHEMISTRY AND PHYSICS, vol. 197, no. 10, October 1996, pages 3209-3228, XP000634281 see page 3211, paragraph 4 - page 3213, paragraph 1 see page 3213; figure 2 ---	15
Y	WO 91 12285 A (EXXON CHEMICAL PATENTS INC) 22 August 1991 see claims 1,2 see page 30, line 11 - line 13 see example 1	15,16
X	see page 37, line 21; example 10 ---	37
Y	ST@?VNENG J A ET AL: "Influence of rotation between agostic structures on ethene interaction with a zirconocene polymerization site" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 519, no. 1, 26 July 1996, page 205-208 XP004035900 see page 278; figure 1 -----	15,16

INTERNATIONAL SEARCH REPORT

International application No.
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-14,20,31

Tridentate ligand of formula (I)(R1-X-A-Z-R2)2-, particular compound corresponding to formula (I), metallic complexes comprising this ligand, method of synthesizing a block copolymer with such metallic complexes as precursors.

The technical feature linking these previous claims is the tridentate ligand of formula (I)

2. Claims: 15-19,21-30,32-48

Living block copolymerisation method producing block copolymer with specific features (MWD, proportion of first or second homopolymer incorporated), blocks copolymers having these specific characteristics and living polymerisation method.

The technical feature linking these claims is the living polymerisation method.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/07466

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9742197 A	13-11-1997	AU 2780197 A	26-11-1997
WO 9421700 A	29-09-1994	US 5391629 A	21-02-1995
		CA 2158868 A	29-09-1994
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